



Supporting Information

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

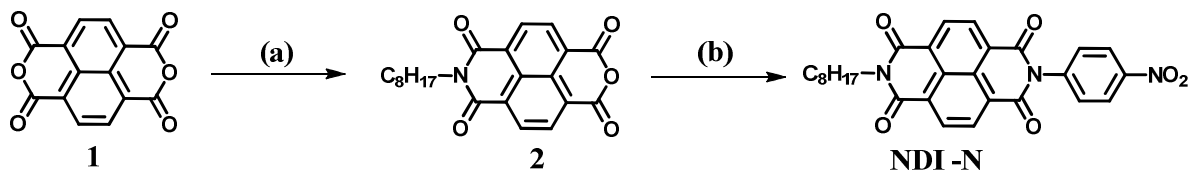
Effect of Amide Hydrogen Bonding Interaction on Supramolecular Self-Assembly of Naphthalene Diimide Amphiphiles with Aggregation Induced Emission

Namdev V. Ghule,^[a] Duong Duc La,^[b] Rajesh S. Bhosale,^[a] Mohammad Al Kobaisi,^[b]
Aaron M. Raynor,^[b] Sheshanath V. Bhosale,^{*[b]} and Sidhanath V. Bhosale^{*[a]}

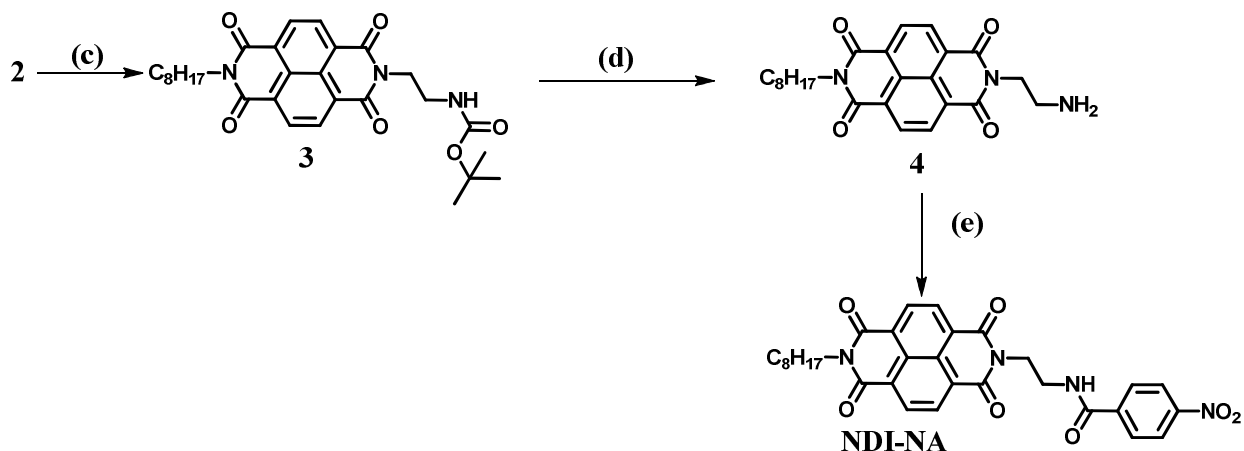
open_201500201_sm_miscellaneous_information.pdf

Supporting Information

A)



B)



Scheme S1. Synthesis of naphthalene diimide amphiphiles; Reagents and conditions:

A) (a) *n*-propanol+H₂O (1:1), octyl amine, 50 °C, 24 h, N₂ atm., 74%, (b) 4-nitroaniline, DMF, reflux, 12 h, N₂ atm., 70%; B) (c) mono boc-ethylenediamine, Et₃N, *i*PrOH, 72 h, 90 °C, 78%, (d) TFA:DCM (1:1), 3h, 96%, (e) SOCl₂, DMF, 4-Nitro benzoic acid, DCM, Et₃N, 12 h, r.t., 62%.

Synthesis of compound 2

In a 100 mL round bottom flask, water (10 mL) and *n*-propanol (10 mL) 1:1 stir for 10 min at rt under N₂ atm. to this add 1,4,5,8-naphthalenetetracarboxylic dianhydride (1g , 3.73 mmol). Add the octyl amine (2 mL, 1.56 g, 12 mmol, excess) to the above

suspension with constant stirring. Then the suspension was heated at 50 °C and stops the heating after 24 h to give a white precipitate. The reaction mixture was cooled down to rt and acidified using 1 M HCl to pH 1 yields more precipitate. To avoid emulsion formation vigorous stirring is continued for an hour. Then the reaction mixture was filtered and subjected for reflux in acetic acid (excess) for 1h gives wine red clear solution, which was cooled at rt. The obtained precipitate was diluted by DCM (200-300 mL) and then adds H₂O, there was chance for the formation of inseparable solution (this stage keep off by addition of more acetic acid).The organic layer was dried using anhydrous Na₂SO₄ and then reduced in volume under vacuum. To this solution add ethanol (50 mL) followed by evaporation of DCM gave a suspension of the product in ethanol. That was filtered off and washed with ethanol, hexane and small amount of ether to yield: 74% of compound 2.¹H-NMR (300 MHz, CDCl₃, TMS): δ (ppm) 8.82 (s, 4H), 4.22-4.17 (t, 2H), 1.79-1.69 (t, 2H) 1.41-1.26 (m, 10H), 0.89-0.85 (t, 3H); ¹³C NMR (75 MHz, CDCl₃, TMS): δ (ppm) 162.12, 158.80, 133.12, 131.14, 127.88, 126.54, 41.16, 31.73, 29.20, 27.95, 26.99, 22.57, 14.04. Elemental Analysis calcd for C₂₈H₂₅N₃O₆: C, 67.33; H, 5.04; N, 8.41 and found C, 67.34; H, 5.04; N, 8.43.

Synthesis of NDI-N

4-Nitroaniline (0.200 gm, 1.45 mmol) and compound 2 (0.5 gm, 1.319 mmol) were dissolved in 15 mL dry DMF. The reaction mixture was stirred at 145 °C for 12 h under N₂ atmosphere to form dark brown color solution. The heating was stopped and the reaction mixture was cooled at ambient temperature. The solvent was evaporated under reduced pressure using a rotary evaporator. The obtained residue was purified by column chromatography using silica gel (60-120 mesh; SiO₂) as stationary phase,

CH₂Cl₂: MeOH (97:3) as a eluent to get the compound NDI-N, 0.55 g as a white solid (yield:70%). M.P: 230 °C; FT-IR (KBr, cm⁻¹) 1710, 1663, (imide carbonyl symmetric stretching); 1580, 1517 (Nitro functionality) ¹H NMR (CDCl₃, 500 MHz, TMS): δ (ppm) 8.82 (s, 4H), 8.45-8.44 (d, 2H, *J*=9.00), 7.56-7.54 (d, 2H, *J*=8.85Hz), 4.23-4.20 (t, 2H, *J* = 7.62Hz), 1.79-1.73 (m, 2H), 1.38-1.28 (m,10H), 0.89-0.86 (t, 3H, *J* = 6.7Hz); ¹³C NMR (CDCl₃, 125 MHz, TMS): δ (ppm) 162.58, 161.53, 147.98, 140.22, 131.65, 131.04, 130.05, 127.34, 124.75, 41.13, 31.77, 29.25, 29.16, 28.05, 22.61, 14.07; ESI-MS: *m/z* cal. C₂₈H₂₅N₃O₆ : 499; Found C₂₈H₂₄N₃O₆ (%): [M-H]⁺ 498; Elemental Analysis calcd for C₂₈H₂₅N₃O₆: C, 67.33; H, 5.04; N, 8.41 and found C, 67.34; H, 5.04; N, 8.43.

Synthesis of compound 3

Mono *boc*-ethylene diamine (0.557 g, 3.482 mmol) and Et₃N (0.35 mL, 3.482 mmol) were added to a mechanically stirred suspension of monooctylnaphthalenediimide (1.20 g, 3.166 mmol) in *i*PrOH (60 mL). The resulting mixture was refluxed for 72 h under N₂ atm. After cooling at rt, white solid was obtained, which was filtered and washed with MeOH. Then the reaction mixture was subjected for purification using column chromatography (60-120 mesh; SiO₂) as a stationary phase and CH₂Cl₂: MeOH (98:2) as a eluent to yield compound 3 as solid 1.3 g (yield: 78%).² M.P: 205 °C; FT-IR (KBr, cm⁻¹):1722, 1704 (imide carbonyl symmetric stretching); 1659 (imide carbonyl asymmetric stretching), 1579 (C=N of pyridine ring); ¹H NMR (500 MHz, CDCl₃, TMS): δ (ppm) 8.77-8.74 (dd, 4H, *J* = 7.6 Hz), 4.87 (br, 1H), 4.39-4.37 (t, 2H, *J* = 5.64 Hz), 4.20-4.17 (t, 2H, *J* = 7.26 Hz), 3.56-3.55 (t, 2H), 1.77-1.71 (m, 2H), 1.30-1.25 (m, 2H) 0.890-0.86 (t, 3H, *J* = 6.7 Hz); ¹³C NMR (125 MHz, CDCl₃, TMS): δ (ppm) = 163.09, 162.66, 156.09, 130.96, 130.80, 126.58, 126.37, 79.22, 40.96,40.60, 39.10, 31.74, 29.64,29.22,

29.13, 28.11, 28.01, 27.04, 22.57, 14.03; ESI-MS: m/z (%): calc for $C_{29}H_{35}N_3O_6Na$ $[M+Na]^+$: 544; found: 544; HRMS (ESI-MS, 70 eV) :m/z(%): calc for $C_{29}H_{36}N_3O_6[M+H]^+$: 522.25980; found: 522.25986, calc for $C_{29}H_{36}N_3O_6Na [M+H+Na]^+$:544.24172; found: 544.24181.

Synthesis of compound 4

Trifluoroacetic acid (10 mL) was added dropwise to a stirred suspension of compound 3 (1g, 1.91 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The resulting brown solution was stirred for 3 h at rt. The solvent was removed under reduced pressure by rotary evaporator. The residue was treated with n-hexane (3 x 50 mL) to remove excess of TFA under reduced pressure to afford a white solid of compound 4, 0.77 g (yield: 96%).² The obtained compound **4** was used in next step. M.P: 220 °C; FT-IR (KBr, cm^{-1}) :3446, 2924 (-CH stretching), 1702, (imide carbonyl symmetric stretching); 1658 (imide carbonyl stretching), 1578 (C=N of pyridine ring); 1H NMR (300 MHz, $CDCl_3$ +DMSO- d_6 , TMS): δ (ppm) = 8.64 (s, 4H), 8.50 (br, s, 2H), 5.26 (t, 2H), 4.44 (t, 2H), 4.11(t, 2H), 1.64 (m, 2H), 1.11(m, 10H), 0.80 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ +DMSO, TMS): δ (ppm) = 163.13, 162.50, 130.31, 126.30, 37.75, 37.40, 31.13, 28.59, 28.46, 27.26, 26.42, 21.98, 13.84; ESI-MS: m/z (%): calc for $C_{24}H_{27}N_3O_4[M+H]^+$: 422; found: 422; HRMS (ESI-MS): m/z(%) calc. for $C_{24}H_{28}N_3O_4[M+H]^+$: 422.20578; found: 422.20743.

Synthesis of NDI-NA

In a 50 mL round bottom flask containing 4-nitro benzoic acid (0.147g, 1.06 mmol) add drop by drop distilled thionyl chloride (7.5 mL, 25 mmol) and catalytic amount of distilled DMF with vigorous stirring. The reaction mixture was refluxed for 6 h under N₂ atm. After 12 h, excess of thionyl chloride was removed by evaporation under reduced pressure under N₂ atm. On the other hand in another round bottom flask compound 3 (0.3 g, 0.712 mmol) was dissolved in 25 mL CH₂Cl₂ and to this solution (brown turbid) add TEA 0.4 mL with vigorous stirring, which gives clear reaction mixture. The obtained solution was added drop by drop to the 4-nitro benzoic acid chloride under N₂ atm. The reaction mixture was set to vigorous stirring at r.t. and the reaction progress was monitored using TLC. The reaction was completed in 10 h. The solvent was evaporated under reduced pressure using rotary evaporator under vacuum. The obtained residue was extracted by CH₂Cl₂ (2 x 25 mL) and the organic layer was washed with saturated NaHCO₃ (2 x 10 mL) to remove unreacted acid as well as remaining acid and acid chloride. Then the organic layer was dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure by rotary evaporator, crude product was purified by column chromatography using silica gel as the stationary phase and MeOH: CH₂Cl₂ (97:3) as the eluent to yield the pure product NDI-NA as a white solid 0.28 g (yield:62%). M.P: 295 °C; FT-IR (KBr, cm⁻¹): 3280 (-NH stretching), 2922(-CH stretching), 1702,1656 (imide carbonyl symmetric stretching);1524 (-NO₂ stretching); ¹H NMR (500 MHz, CDCl₃,TMS): δ (ppm) = 8.83 (d, 4H), 8.31-8.29 (d, 2H, J = 8.69 Hz), 7.86-7.84 (d, 2H, J = 8.54Hz), 7.65 (brs, 1H) 4.63-4.60 (t, 2H, J = 4.88 Hz), 4.22-4.19 (t, 2H, J = 7.26 Hz), 4.00-3.99 (t, 2H), 1.76-1.70 (m,2H), 1.26(m, 10H,), 0.88-0.86 (t, 3H);¹³C NMR (75 MHz, CDCl₃+deutrated TFA, TMS): δ (ppm) = 164.16, 163.05,159.24,

150.02, 138.12, 131.75, 131.40, 128.23, 126.98, 125.82, 124.13, 41.39, 40.58, 39.88, 31.71, 27.92, 2.96, 22.57, 13.99; ESI-MS: m/z (%): calc for $C_{31}H_{30}N_4O_7[M+H]^+$: 571; found: 571; calc for $C_{31}H_{29}N_4O_7Na$; HRMS (ESI-MS, 70 eV): m/z (%) calc. for $C_{31}H_{31}O_7N_4[M+H]^+$: 571.2148; found: 571.2198.

Supporting figures

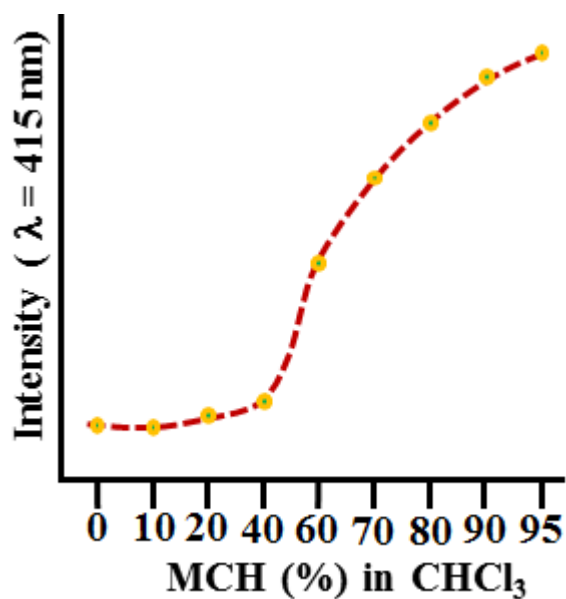


Figure S1. Fluorescence changes of of **NDI-NA** (1×10^{-4} M) with increasing MCH ratio to $CHCl_3$ in solvent mixture at 415 nm wavelength.

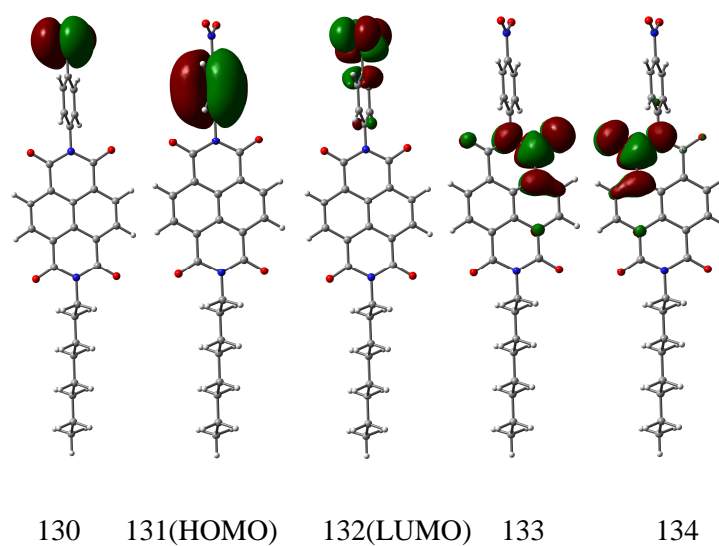


Figure S2. The electron density distribution of HOMO-1, HOMO, LUMO, LUMO+1, and LUMO+2 molecular orbitals of NDI-N.

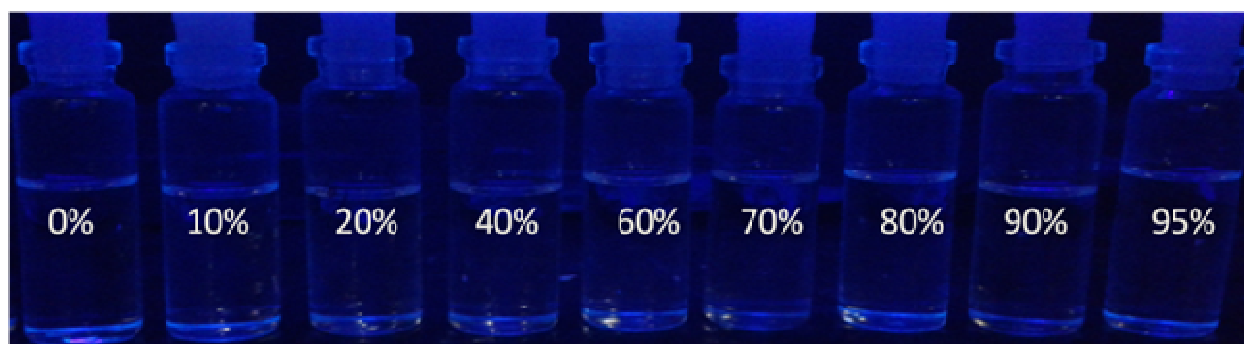


Figure S3. Photographs of **NDI-N** solution in the mixture of CHCl_3 / MCH (v/v; 0-95%) taken under 365 nm hand-lamp irradiation.

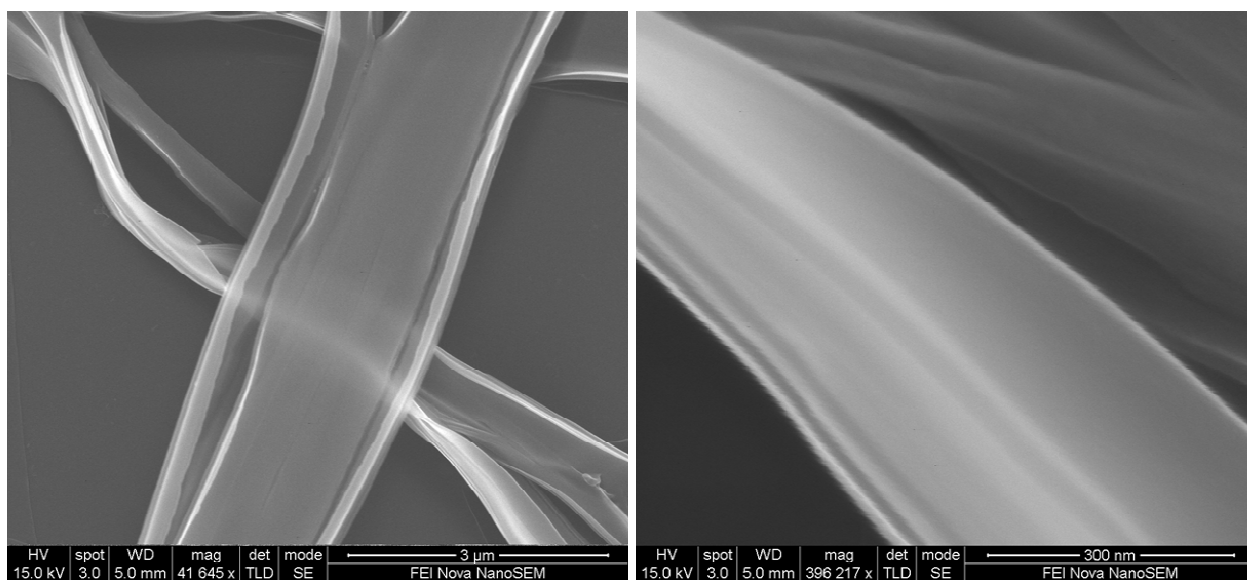


Figure S4. SEM images of the **NDI-NA** in organic solvents such as CHCl_3/MCH (v/v; 10:90%).

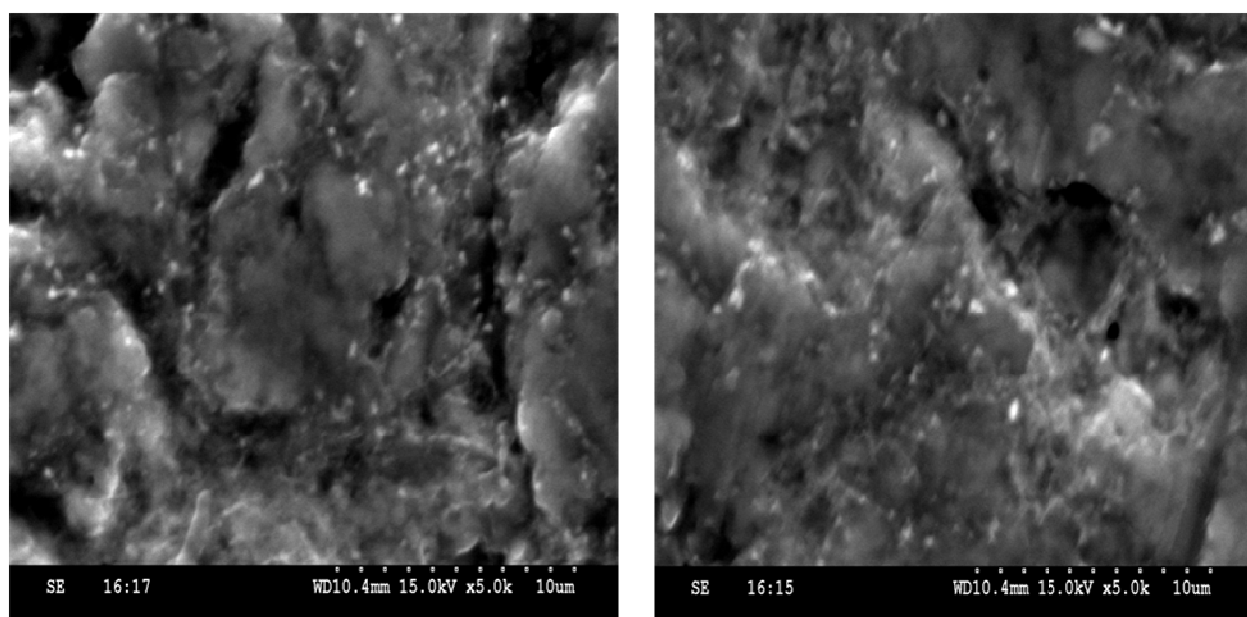


Figure S5. SEM images of the **NDI-N** in organic solvents such as CHCl_3/MCH (v/v; 5:95%).

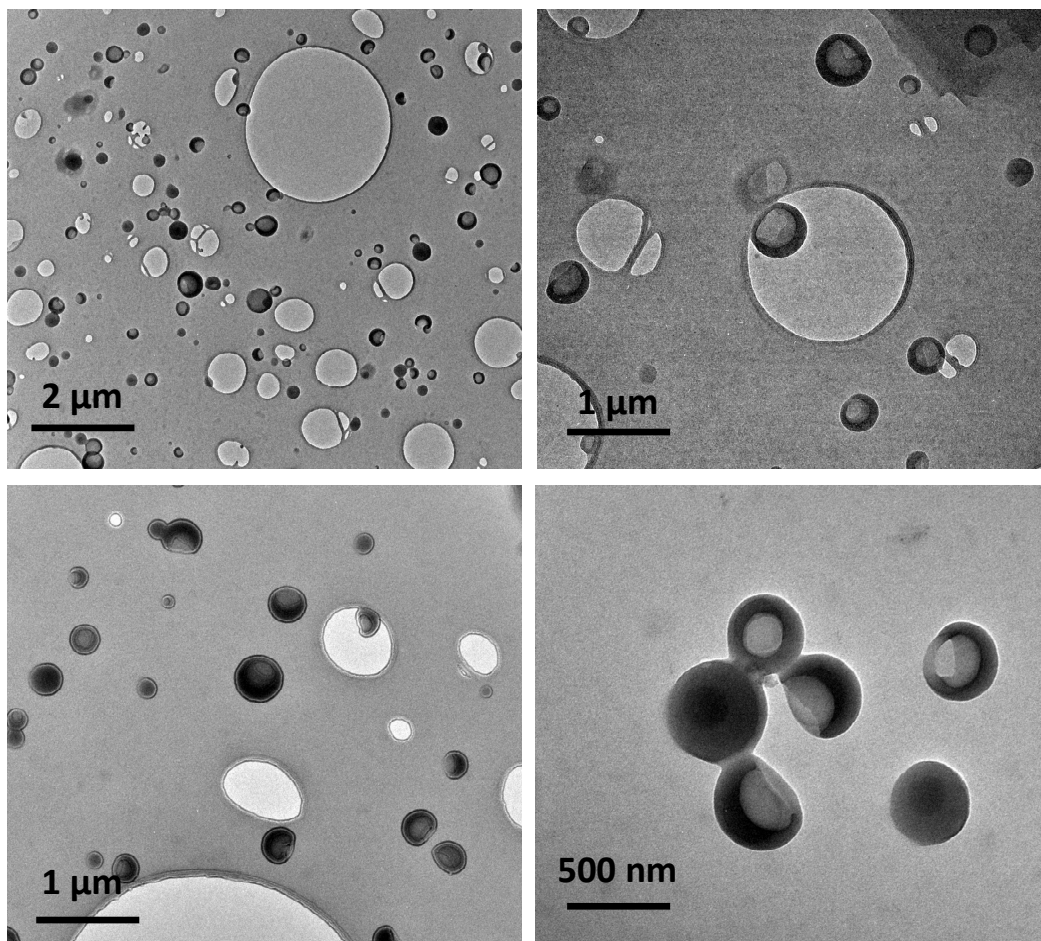


Figure S6. TEM images of the NDI-NA in organic solvents such as CHCl_3/MCH (v/v; 5:95).

Powder X-ray Diffraction (PXRD).

XRD data was recorded on a Seifert XRD3000P diffractometer having a Cu K α radiation source ($\lambda = 0.15406$ nm) operating at a voltage and current of 40 kV and 30 mA, respectively. The self-assembled NDI-NA microsheets in CHCl_3/MCH (5:95, v/v) were drop-casted on a glass slide and allowed to dry naturally via solvent evaporation.

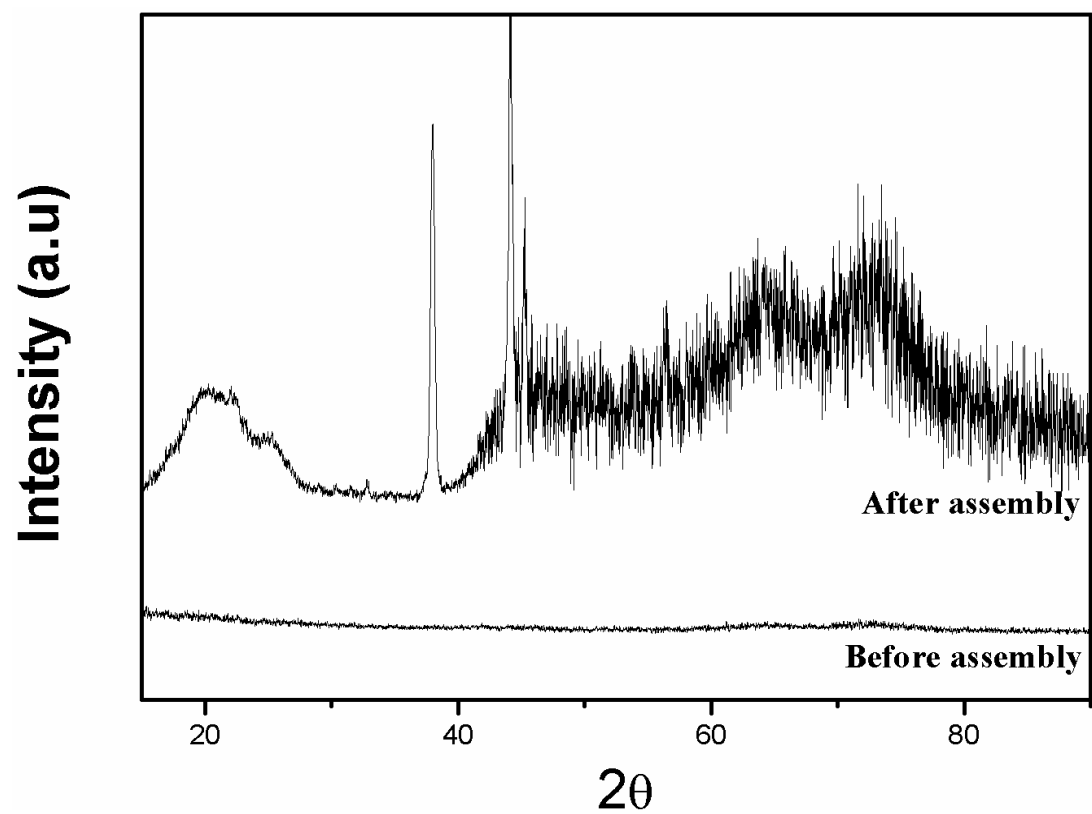


Figure S7. XRD patterns of the **NDI-NA** in assembly state from CHCl_3 : MCH (v/v; 5:95).

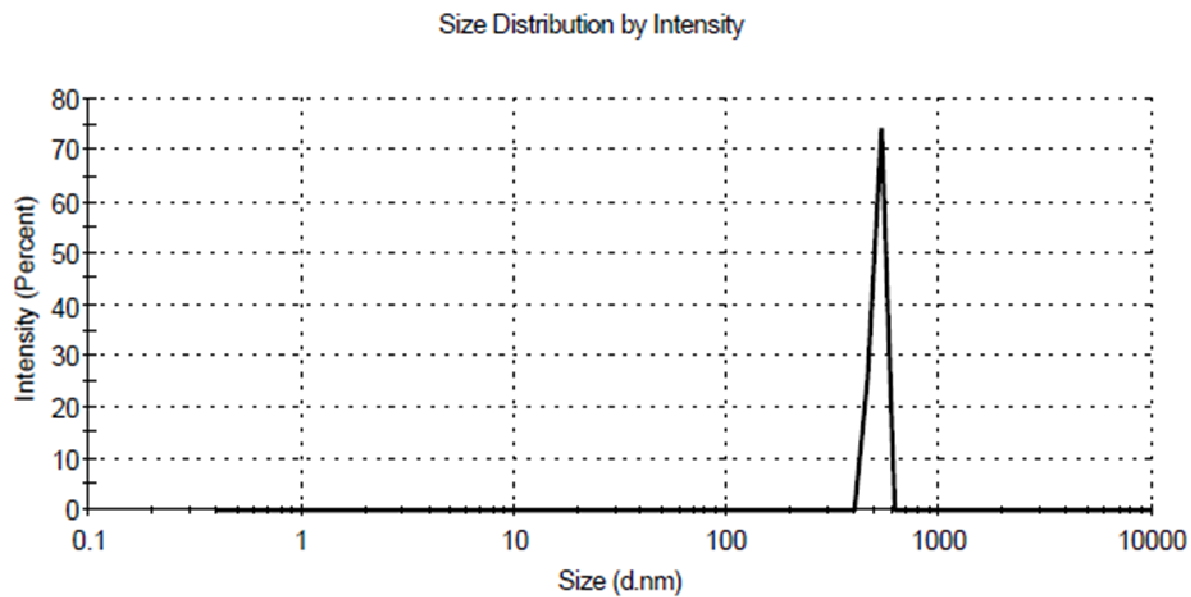


Figure S8. DLS results for **NDI-NA** solution in the mixture of CHCl_3 / MCH (v/v; 5:95%).

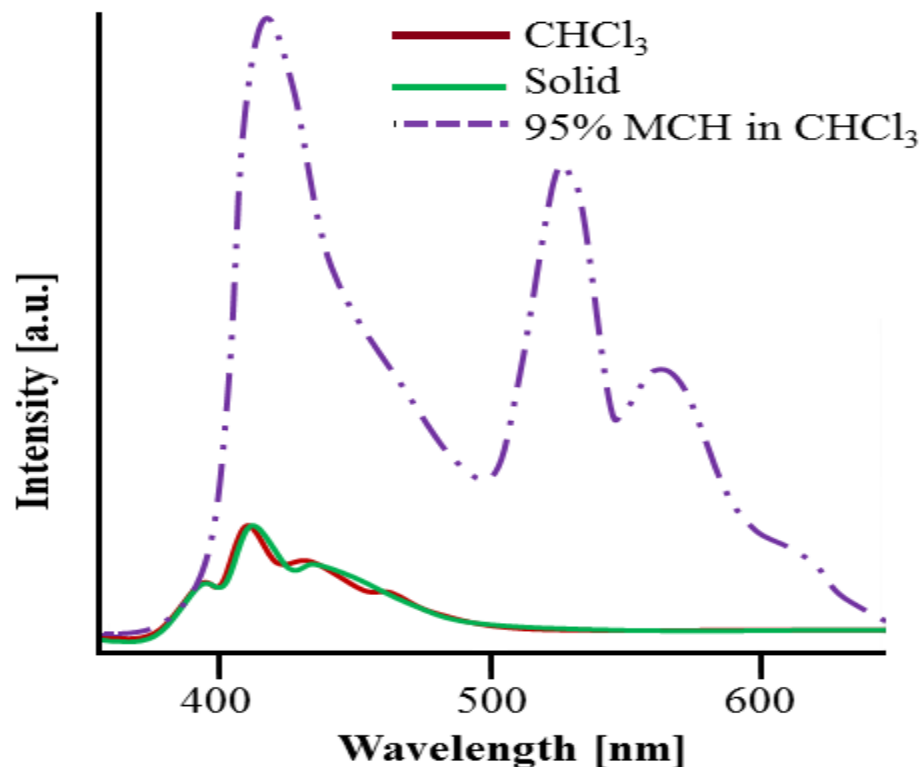


Figure S9. PL spectra ($\lambda_{\text{ex}} = 350$ nm) of **NDI-NA** (1×10^{-4} M) in CHCl_3 , MCH/ CHCl_3 (95:5, v/v) and solid state at room temperature respectively.

Table S1. The electronic excitation energies and the corresponding oscillator strengths and configuration interaction coefficients of the low lying excited states of **NDI-NA**.

Electronic transition	Energy (eV/nm)	f (Oscillator Strength)	Composition	CI (Configuration interaction)
Singlet	2.6453/468.70	0.0012	H \rightarrow L	0.70027
Singlet	2.9061/426.63	0.0002	H-1 \rightarrow L	0.69549
Singlet	3.0215/410.34	0.0001	H-5 \rightarrow L H-4 \rightarrow L	-0.48193 0.49894
Singlet	3.271/379.04	0.0014	H-7 \rightarrow L+1 H-6 \rightarrow L+1 H \rightarrow L+1	0.66424 0.16606 0.10401
Singlet	3.2836/377.59	0.1375	H-8 \rightarrow L H-2 \rightarrow L	0.54506 0.41343
Singlet	3.3218/373.24	0.2725	H-8 \rightarrow L H-2 \rightarrow L	-0.40490 0.55699
Singlet	3.3665/368.29	0.0026	H-10 \rightarrow L H-3 \rightarrow L	-0.27481 0.63814
Singlet	3.4111/363.47	0.0222	H-7 \rightarrow L+1 H-1 \rightarrow L+1 H \rightarrow L+1	-0.12364 -0.14711 0.66535

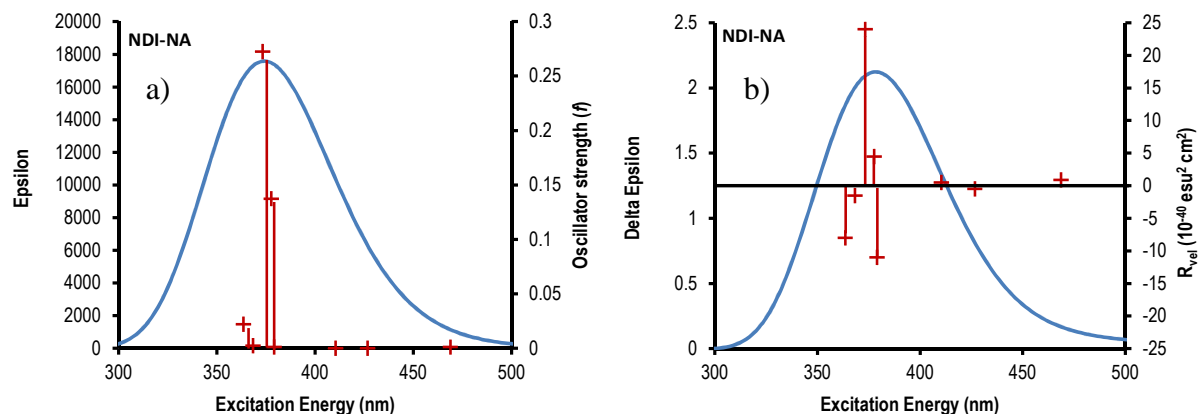


Figure S10. The UV-vis spectrum (a), and the ECD spectrum (b) of NDI-NA as predicted by the TD-DFT/B3LYP/6-311G calculation.

TD-DFT calculation using B3LYP/6-311G level of theory for 8 excitations (electronic transitions) of **NDI-N** in gas phase was conducted using Gaussian 09 suite of programs (Figure) shows that HOMO→LUMO optical transition occurs at 374 nm (3.32 eV) and with very strong oscillator strength $f = 0.4459$. The HOMO – LUMO gap is 350.5 nm or 0.13 hartre.

Table S2. The electronic excitation energies and the corresponding oscillator strengths and configuration interaction coefficients of the low laying excited states of **NDI-N**.

Electronic transition	Energy (eV/nm)	f (Oscillator Strength)	Composition	CI (Configuration interaction)
Singlet	3.0426/407.5	0.0001	H-3 → L	0.53605
			H-2 → L	0.11209
			H-1 → L	0.4202
Singlet	3.1855/389.21	0.0006	H-7 → L	0.10906
			H-6 → L	0.28146
			H-5 → L	0.3069
			H-3 → L	-0.37044
			H-1 → L	0.39723
Singlet	3.2894/376.92	0.0023	H-6 → L+1	-0.44362
			H-5 → L+1	0.52509
Singlet	3.3172/373.76	0.4459	H-4 → L	-0.10554
			H → L	0.68932
Singlet	3.4042/364.21	0.0087	H-8 → L	0.32873
			H-4 → L	0.26235
			H-2 → L	0.52924
Singlet	3.446/359.79	0.0129	H-11 → L	-0.10248
			H-8 → L	0.16842
			H-4 → L	0.52019
			H-2 → L	-0.38209

Singlet	3.4888/355.38	0.0003	H-6 → L	0.38698
			H-5 → L	0.36339
			H-3 → L	0.22315
			H-1 → L	-0.37376
Singlet	3.538/350.44	0.002	H-13 → L	0.10771
			H-8 → L	0.55281
			H-4 → L	-0.30684
			H-2 → L	-0.2029

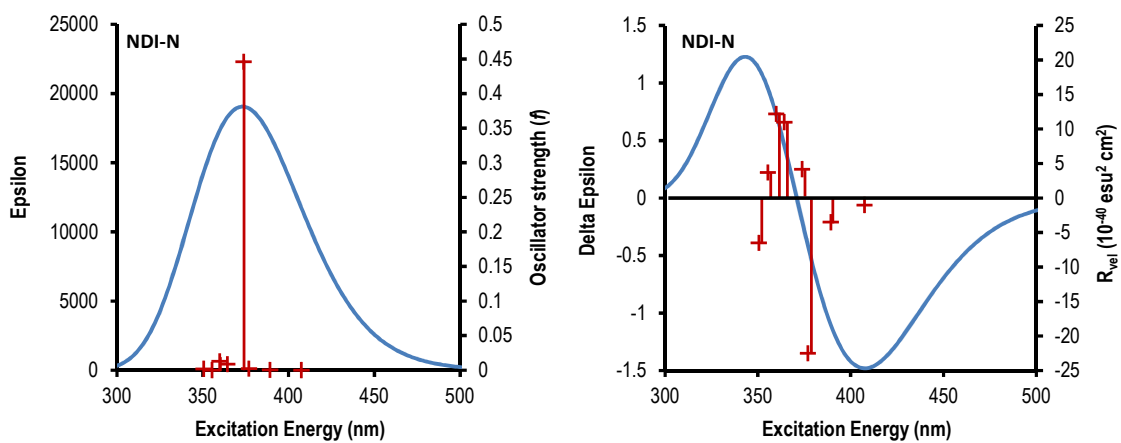


Figure S11. The UV-vis spectrum (a), and the ECD spectrum (b) of NDI-N as predicted by the TD-DFT/B3LYP/6-311G calculation.

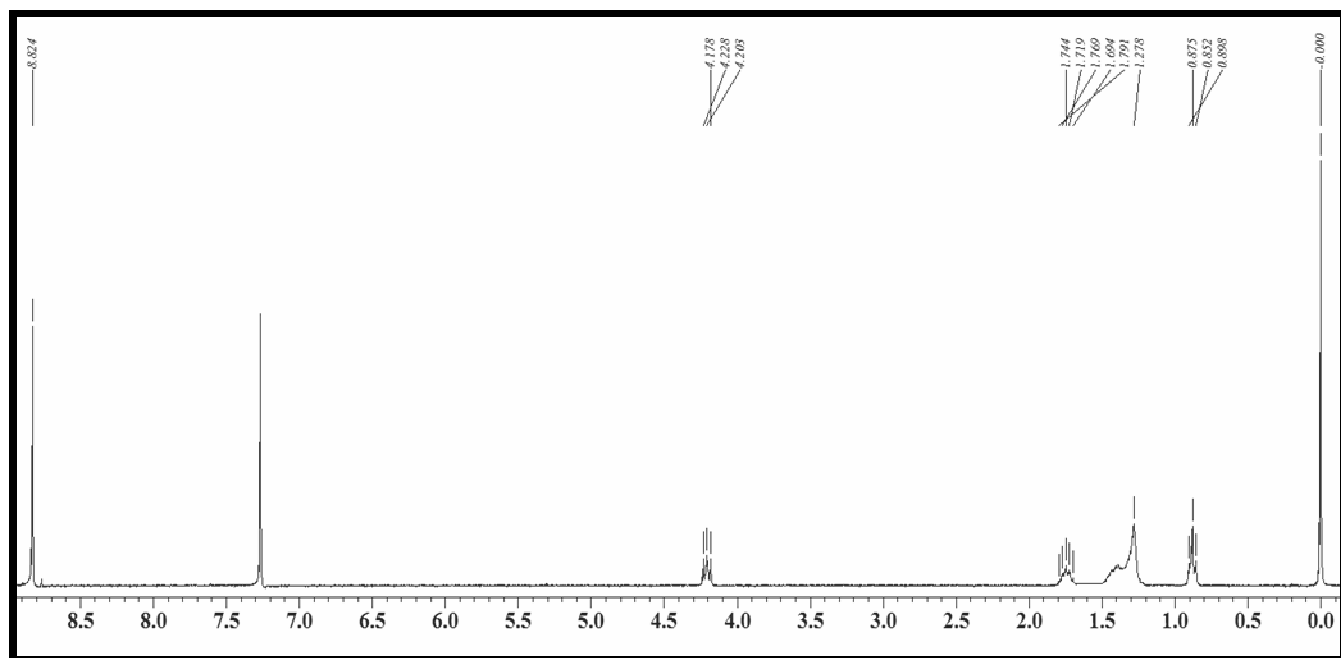


Figure S12. ¹H NMR of compound 2.

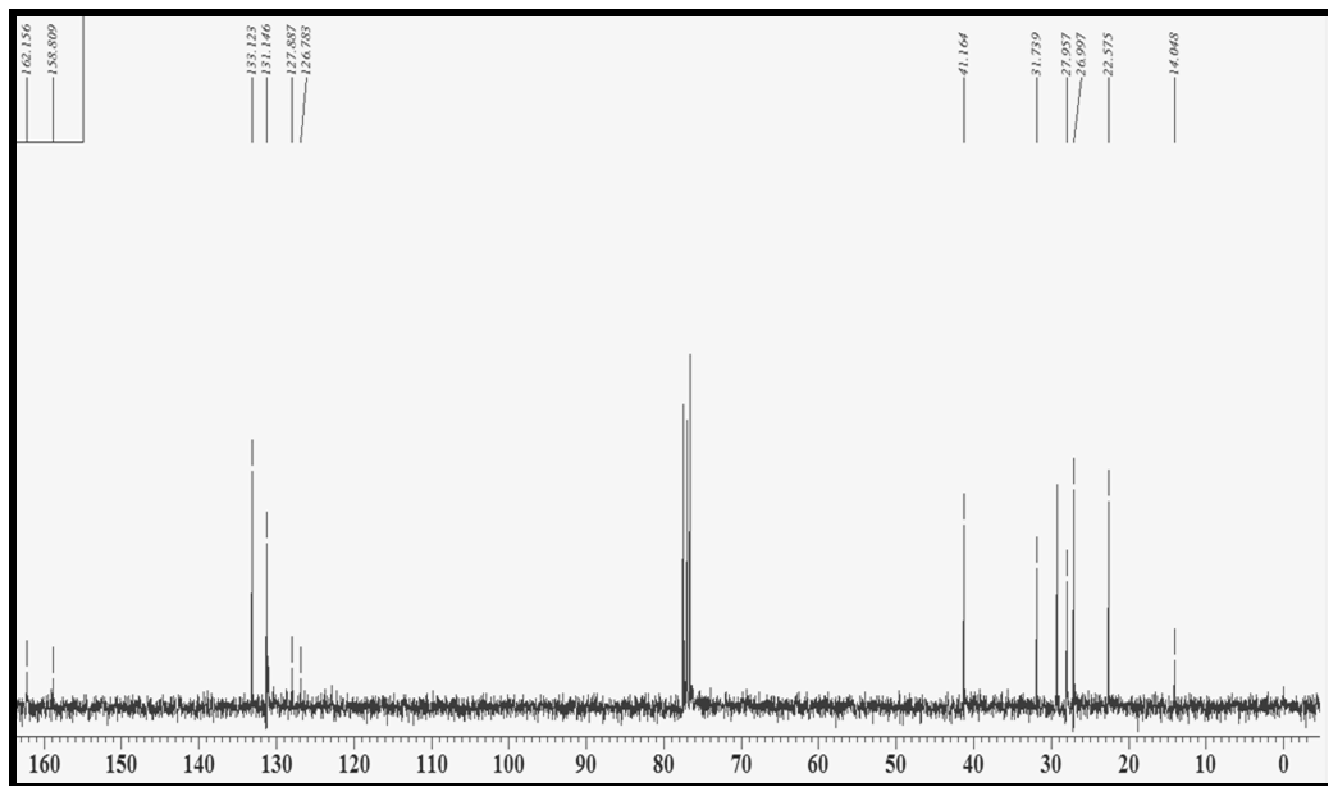


Figure S13. ^{13}C NMR of compound 2

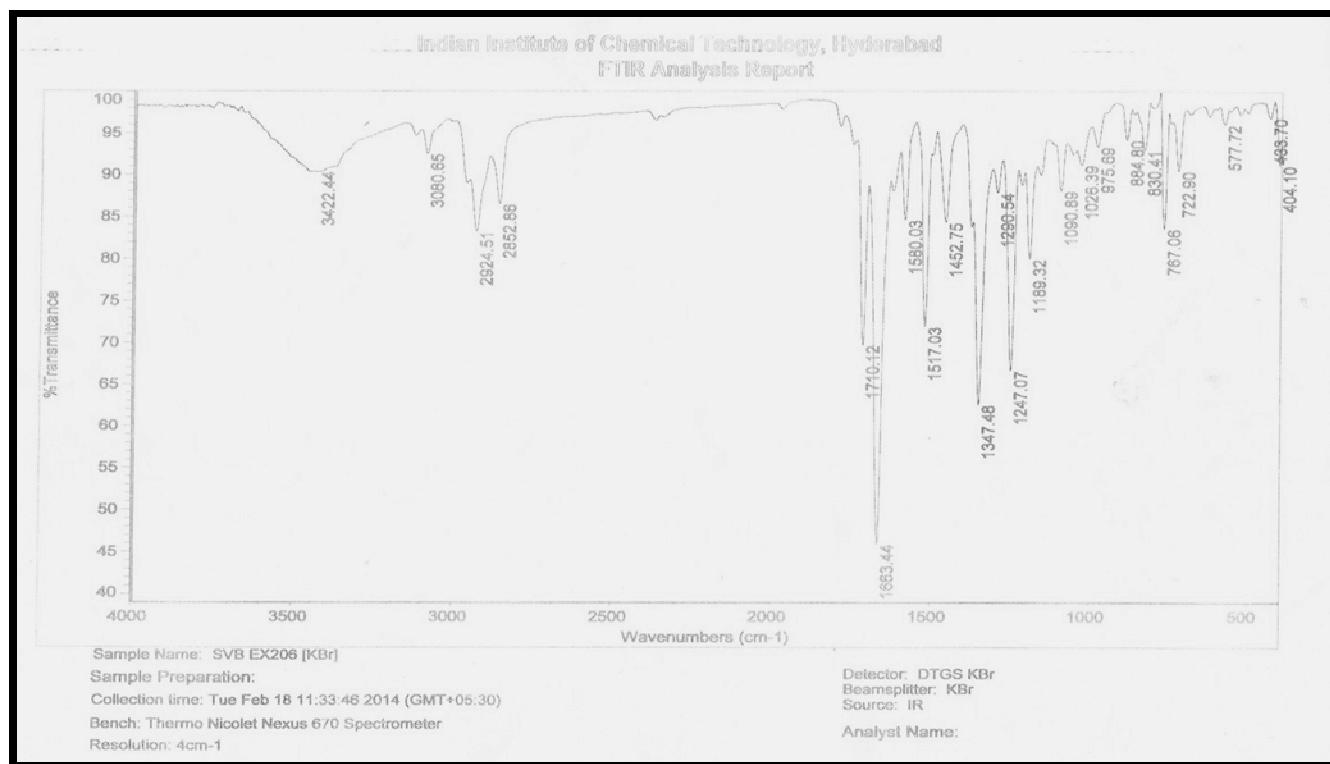


Figure S14. FT-IR of NDI-N

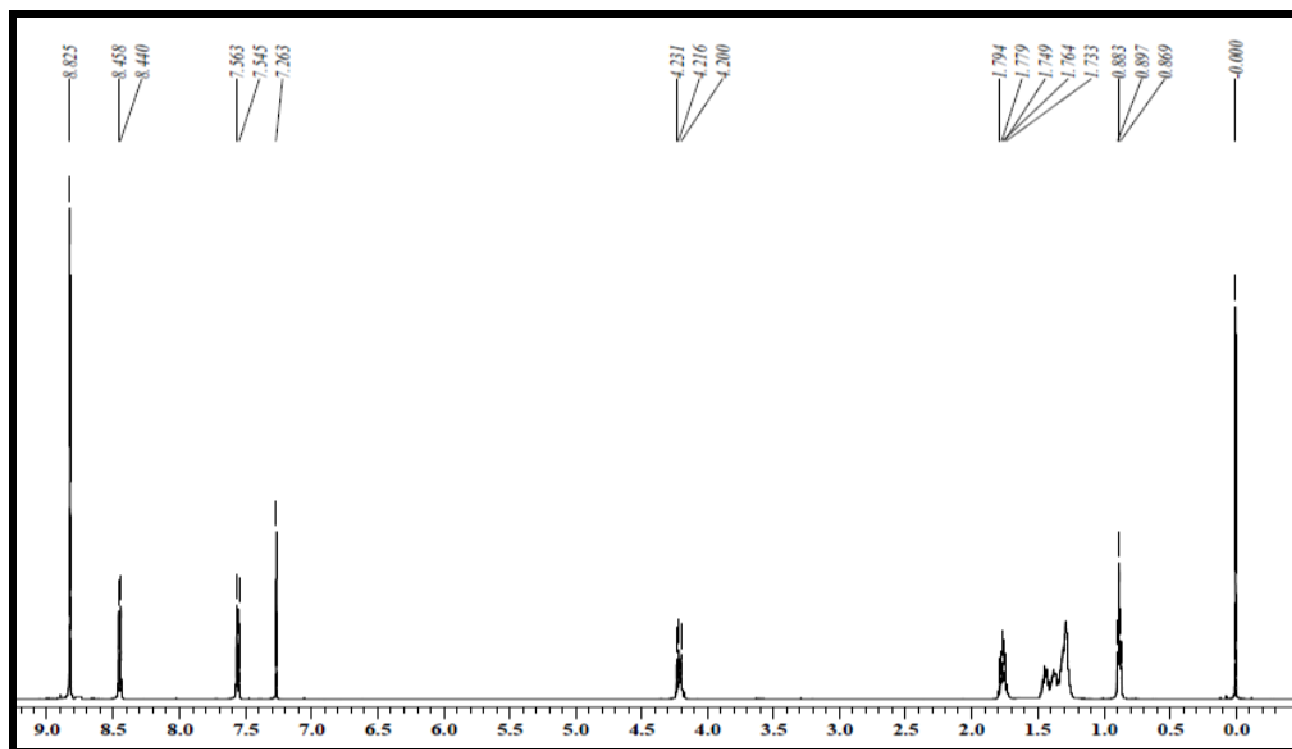


Figure S15. ^1H NMR (CDCl_3) of NDI-N

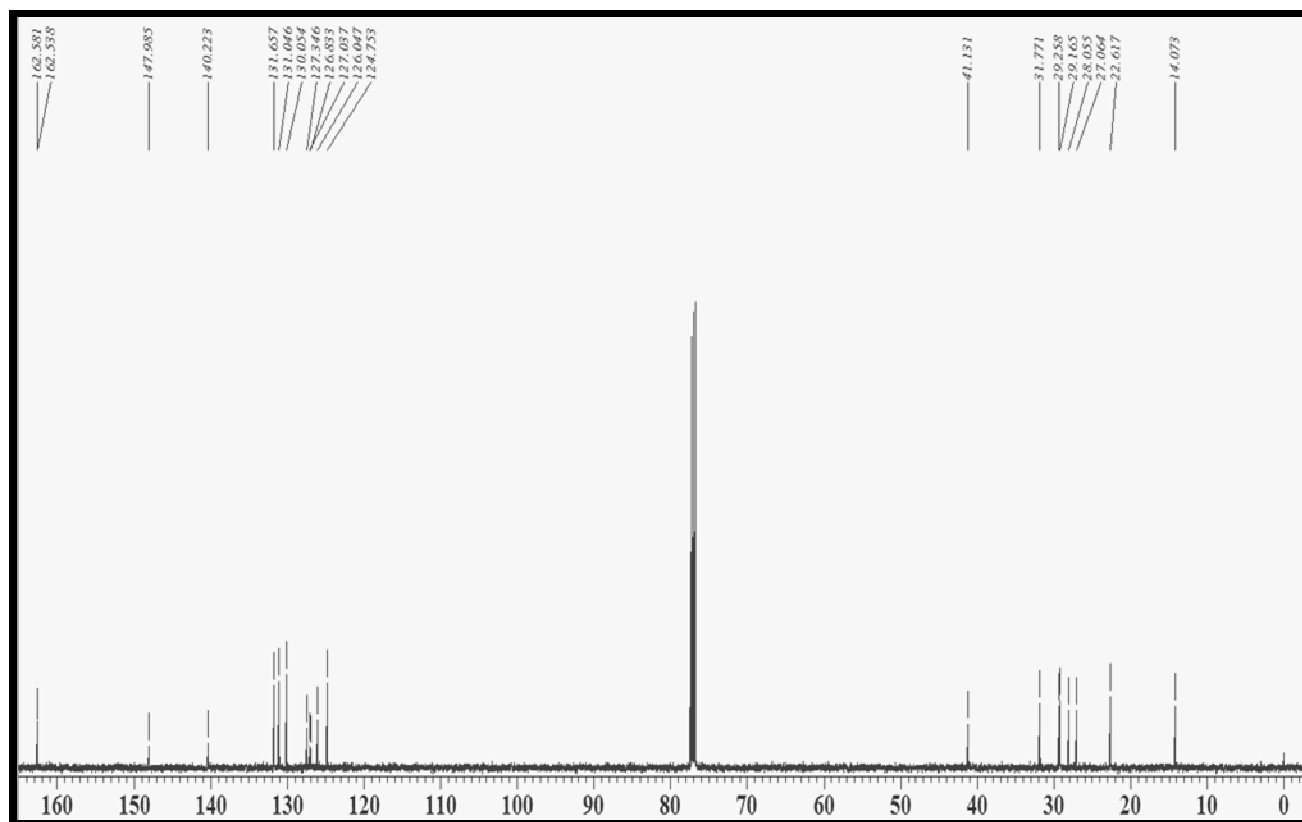


Figure S16. ¹³C NMR (CDCl₃)NDI-N

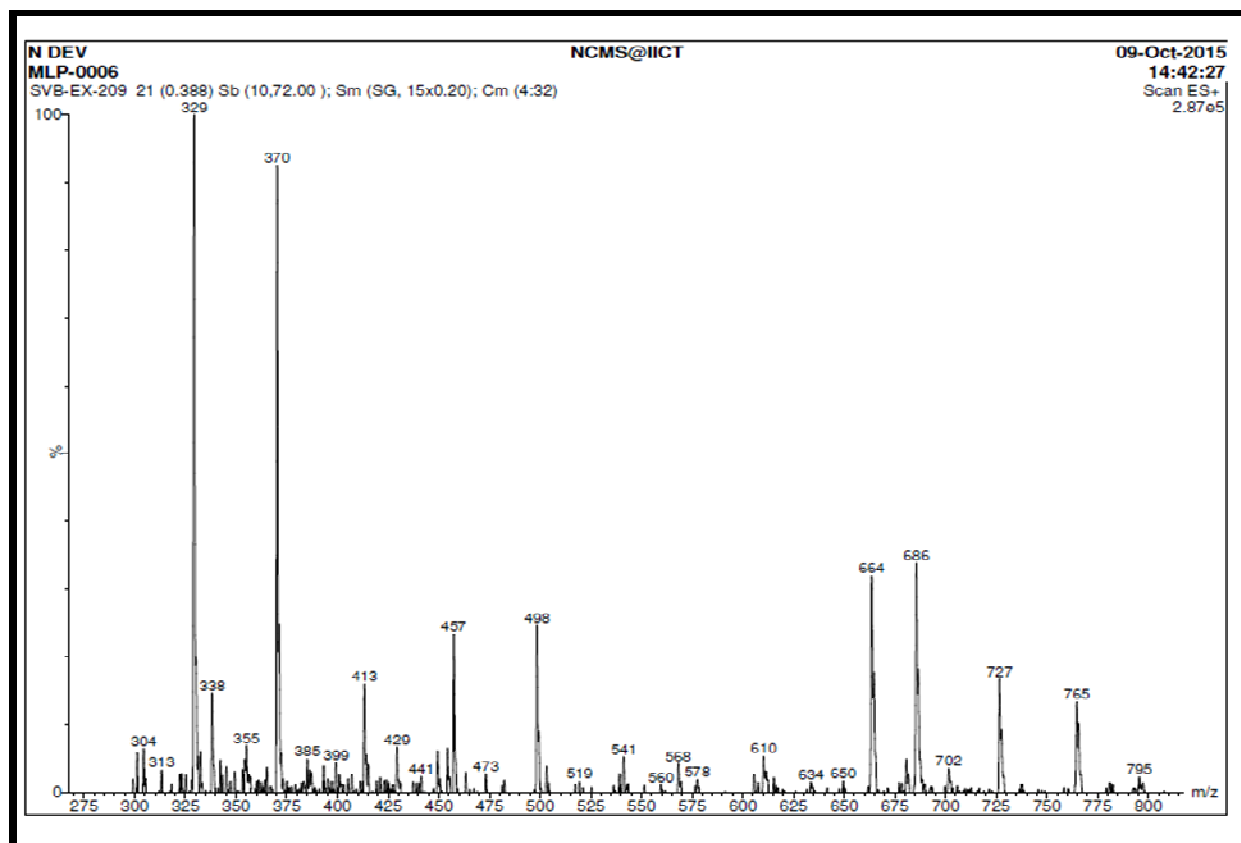


Figure S17. ESI MS (negative mode) compound NDI-N.

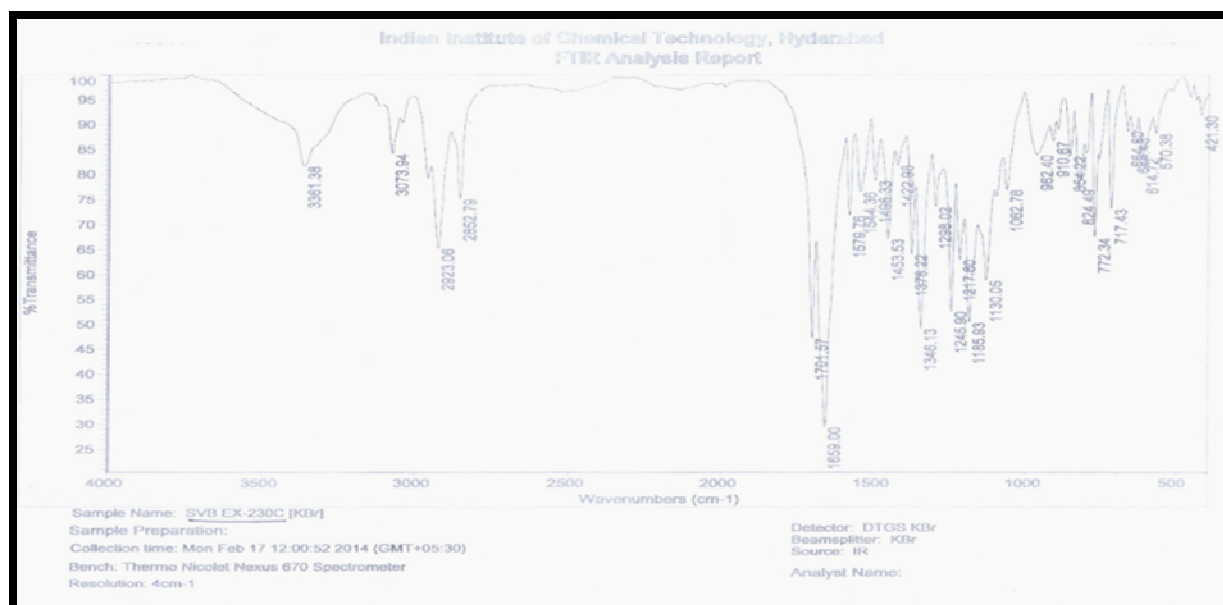


Figure S18. FT-IR of Compound 3.

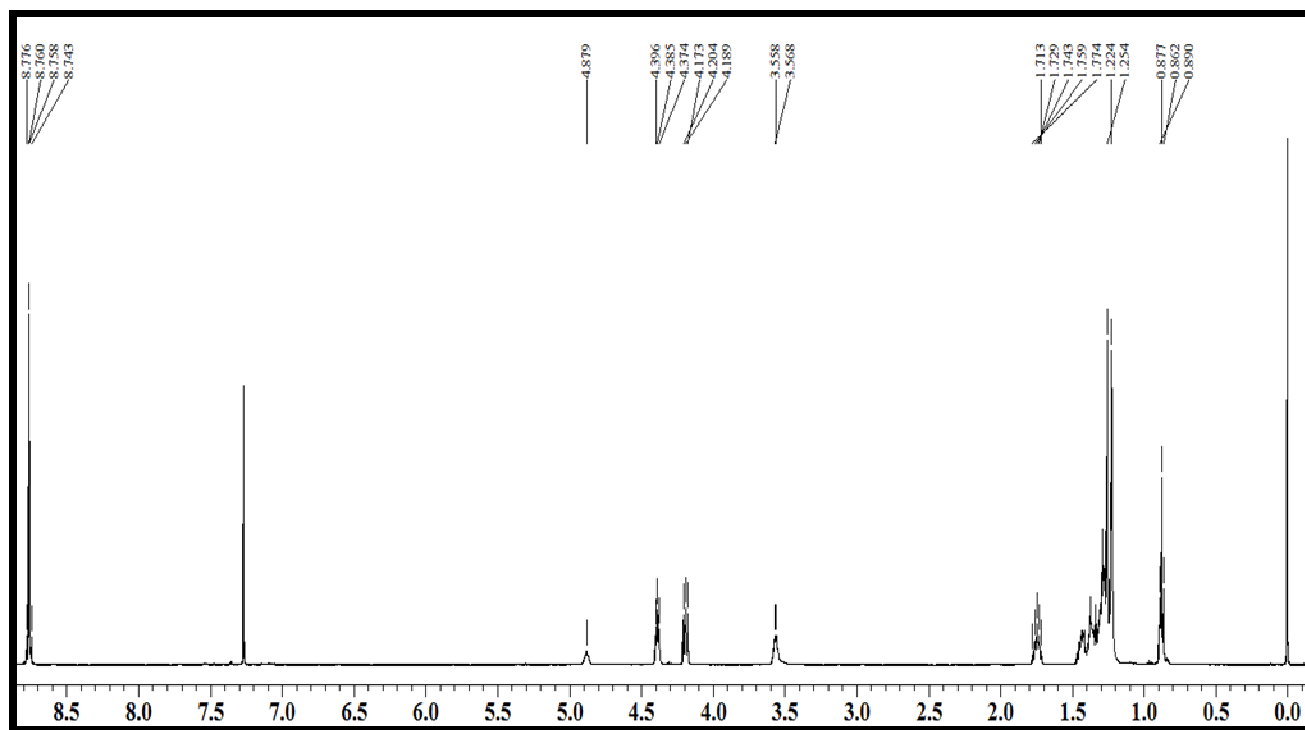


Figure S19. ¹H NMR of Compound 3.

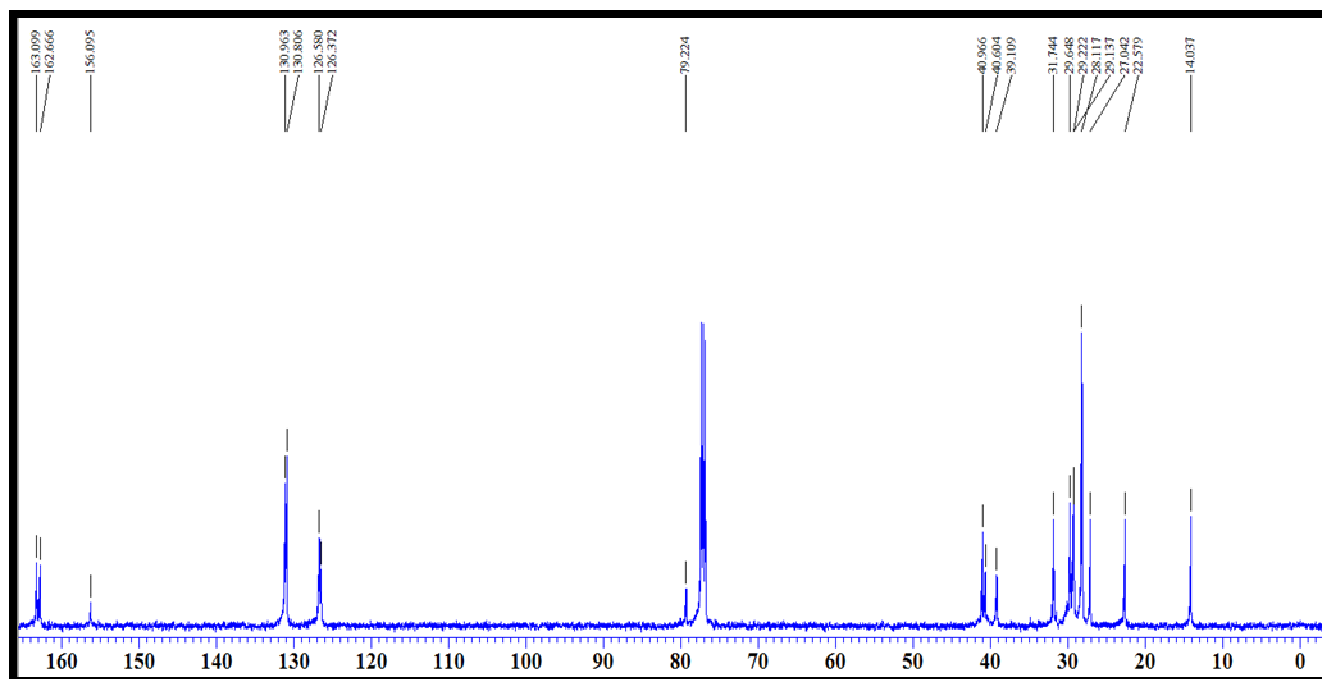


Figure S20. ¹³C NMR of Compound 3.

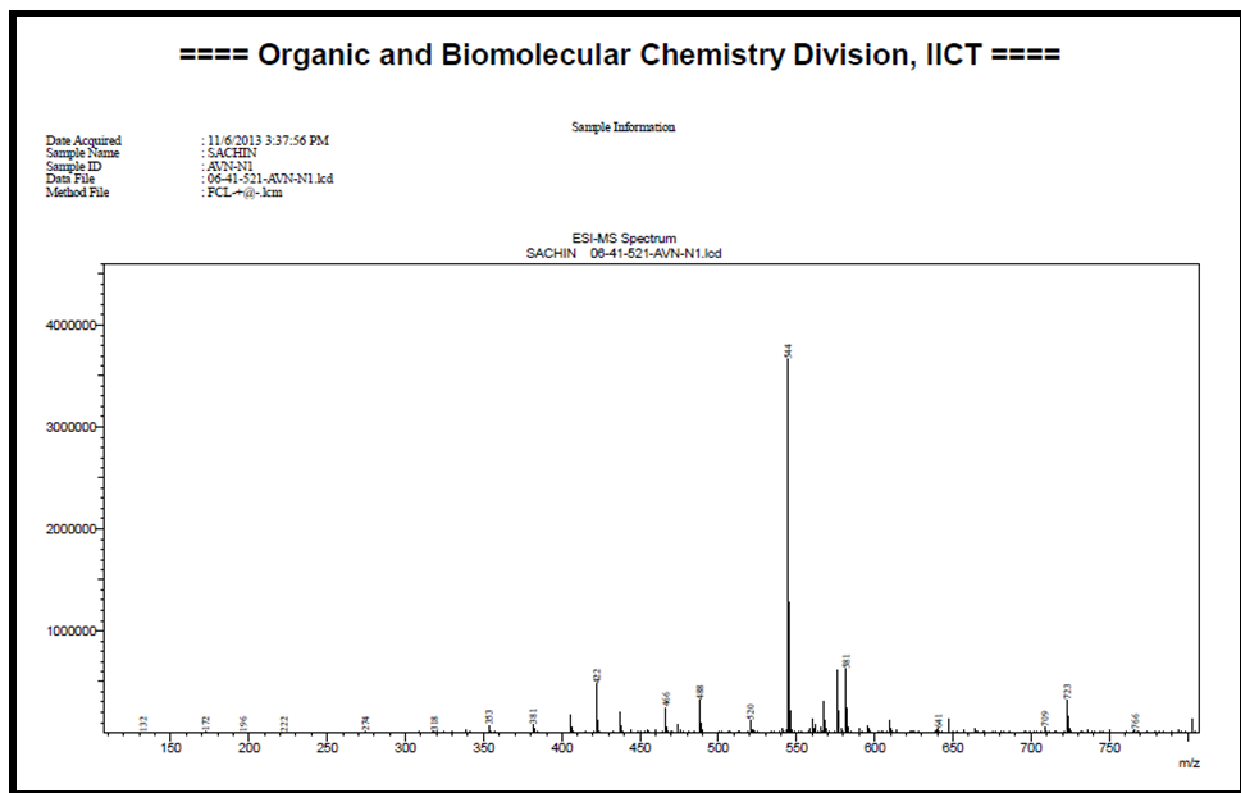


Figure S21. ESI MS Compound 3

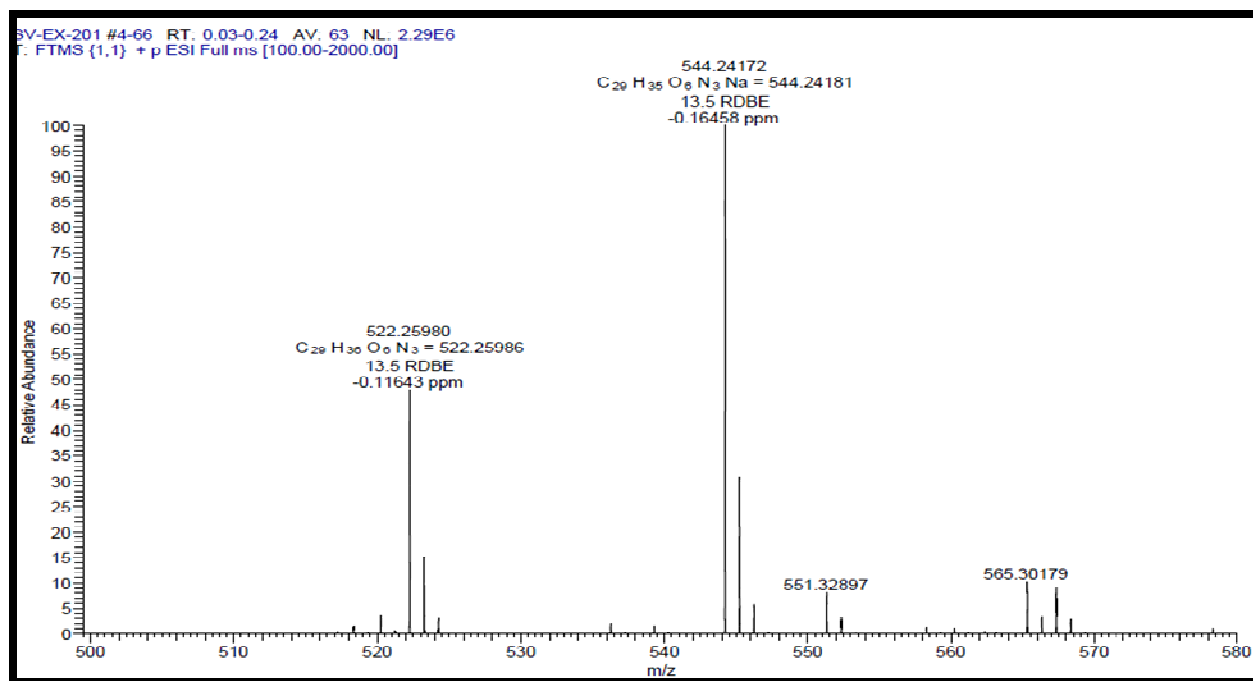


Figure S22. ESI-HRMS of compound 3.

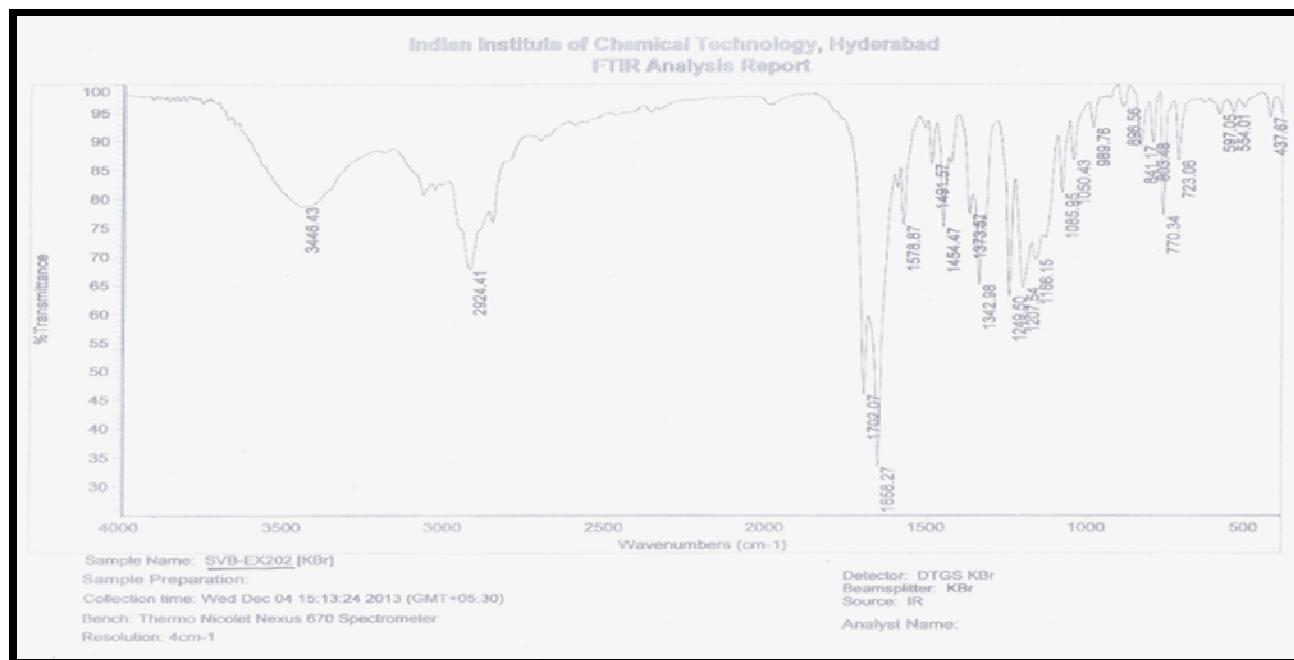


Figure S23. FT-IR of compound of **4**

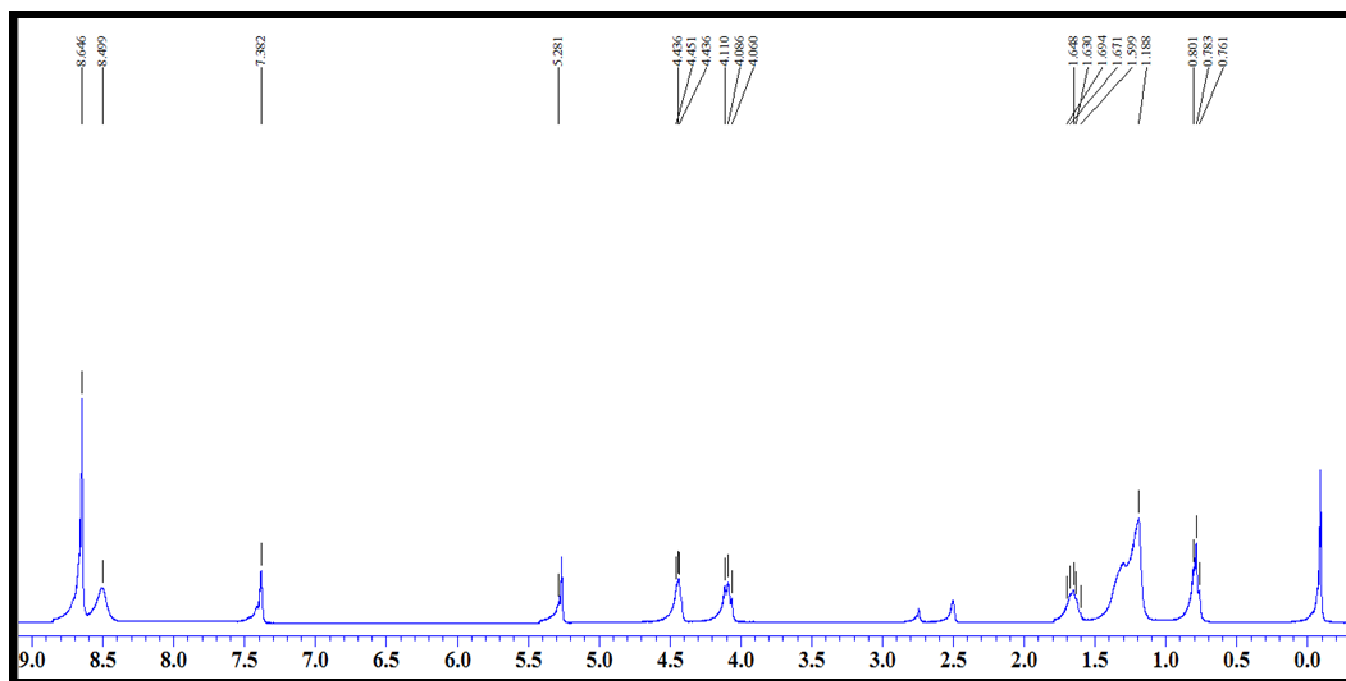


Figure S24. ^1H NMR of compound **4**.

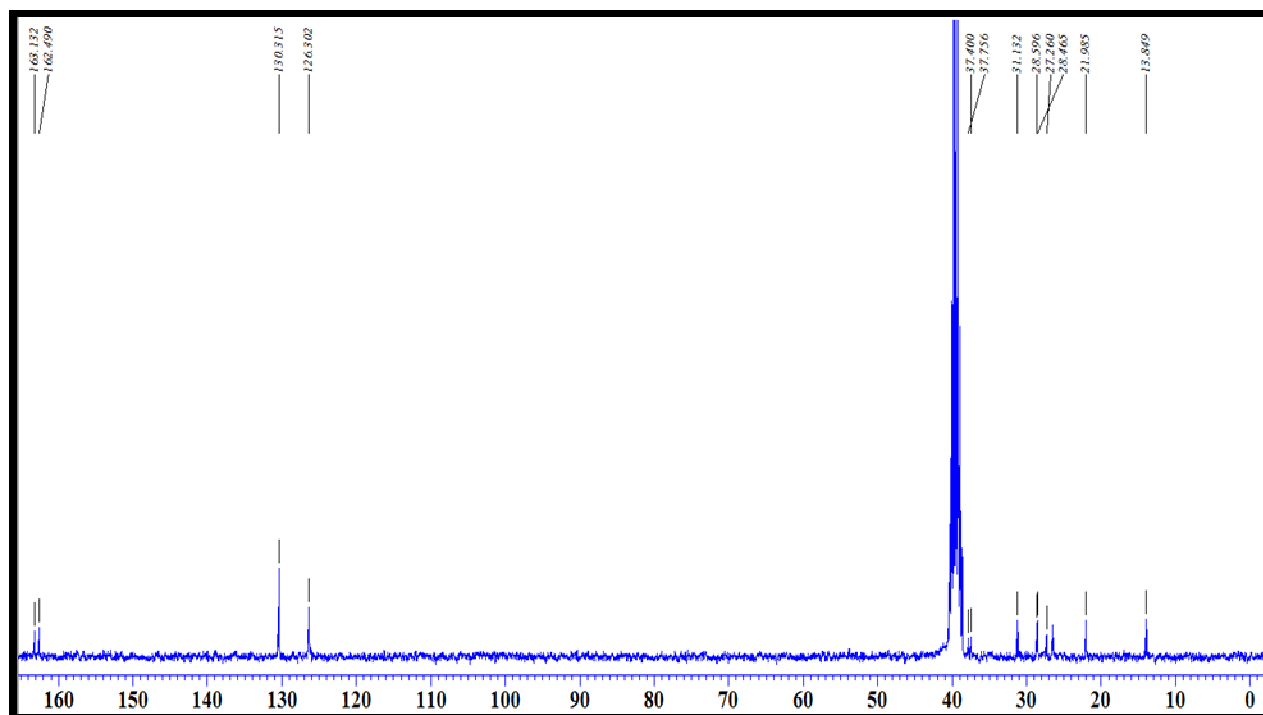


Figure S25. ^{13}C NMR of Compound 4.

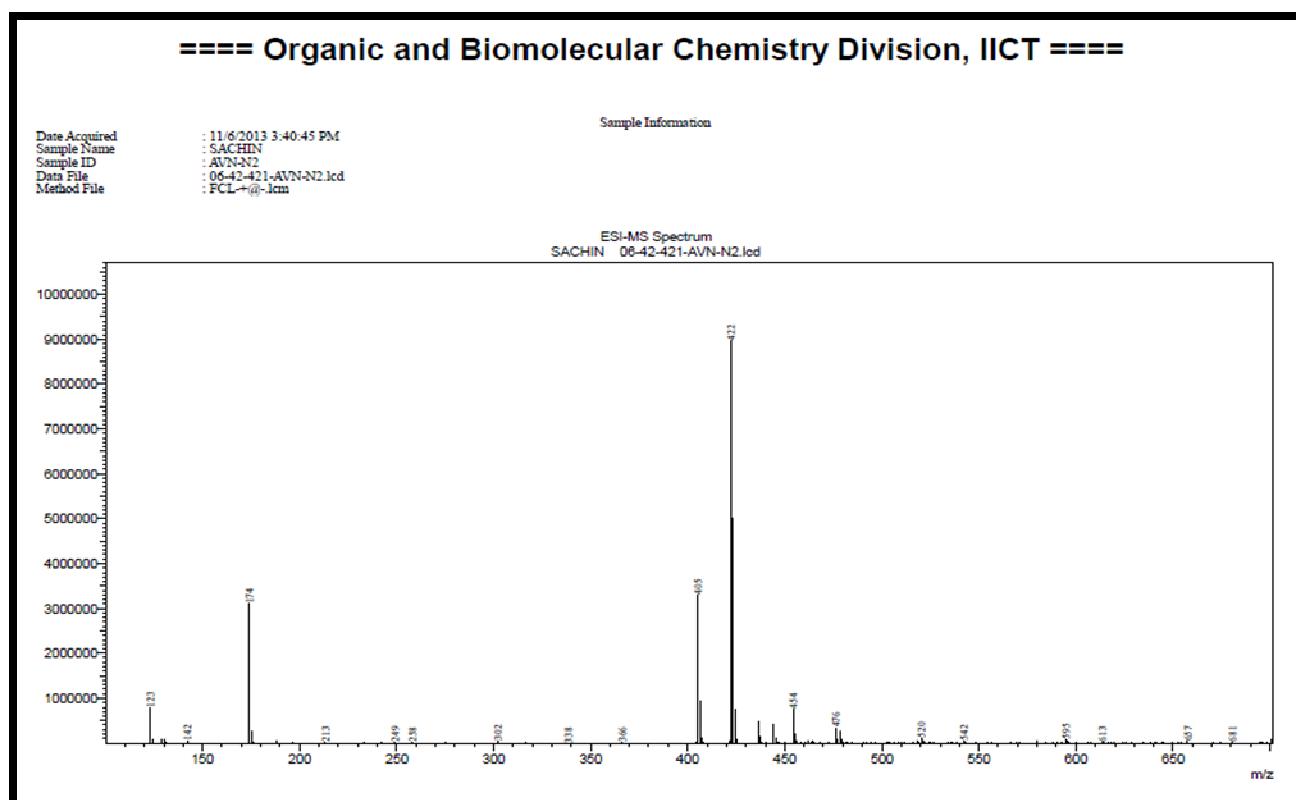


Figure S26. ESI-MS of compound 4.

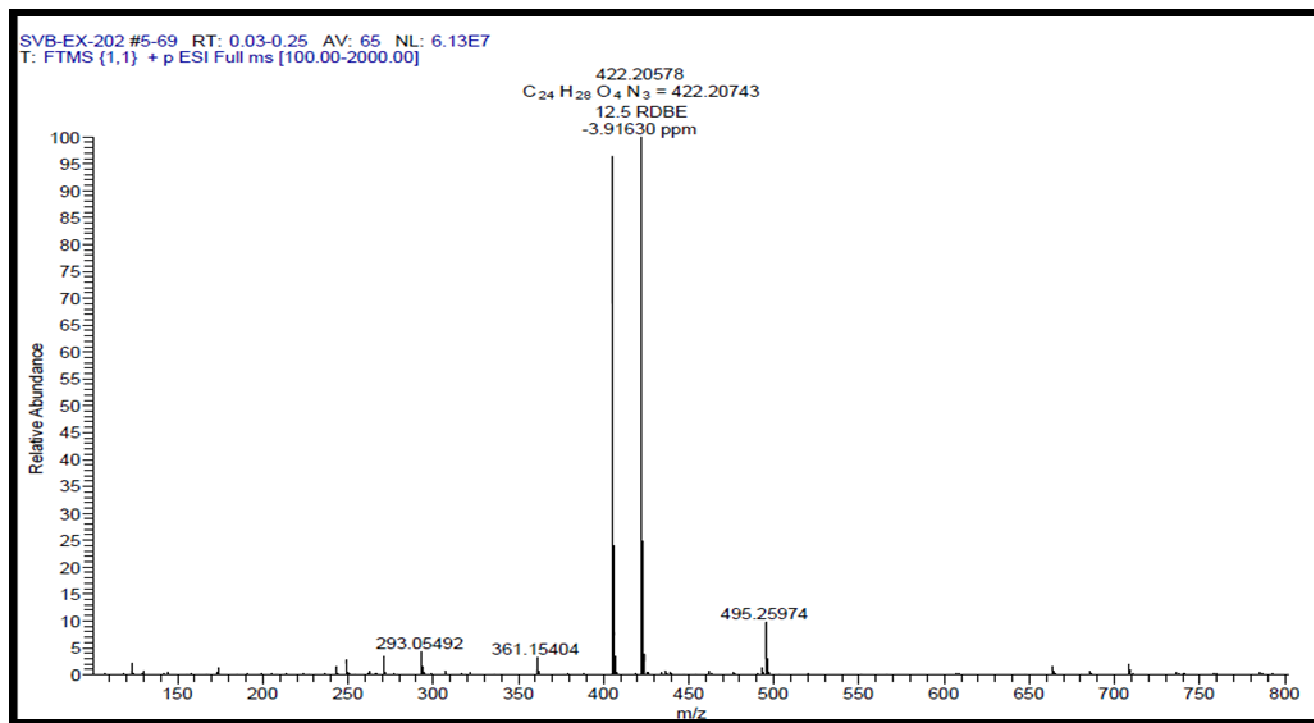


Figure S27. ESI-HRMS of compound 4.

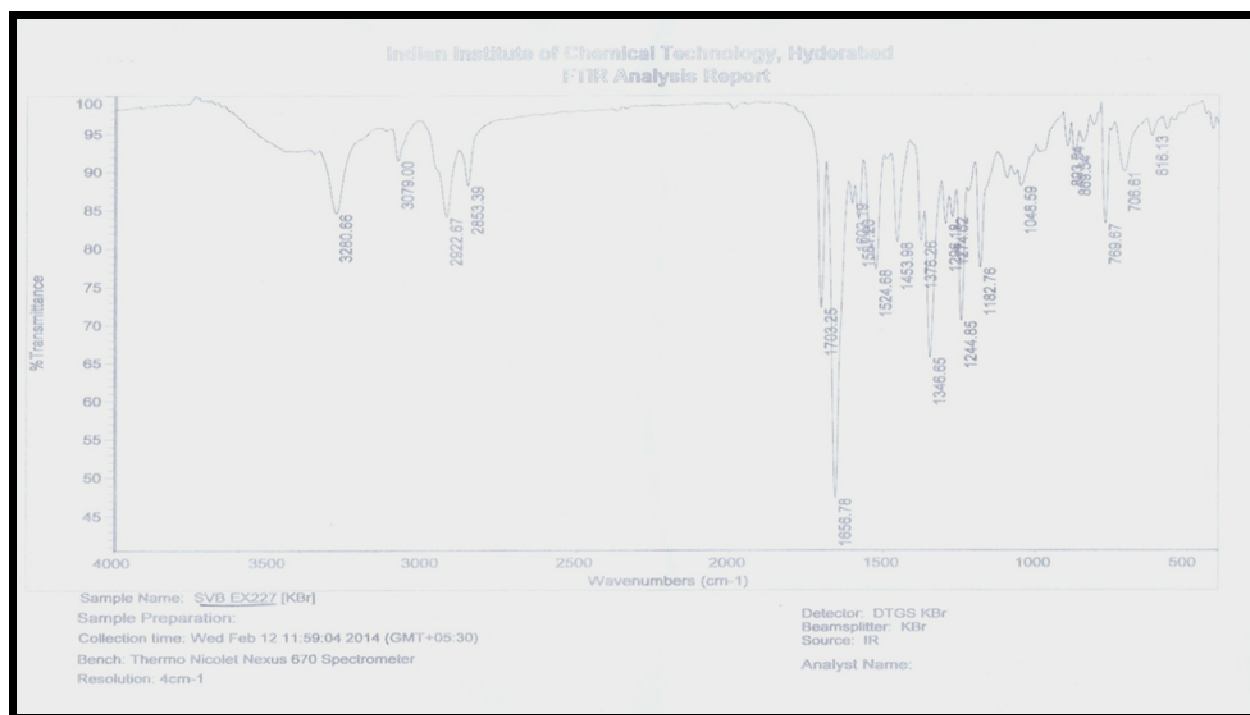


Figure S28. FT-IR spectrum of NDI-NA.

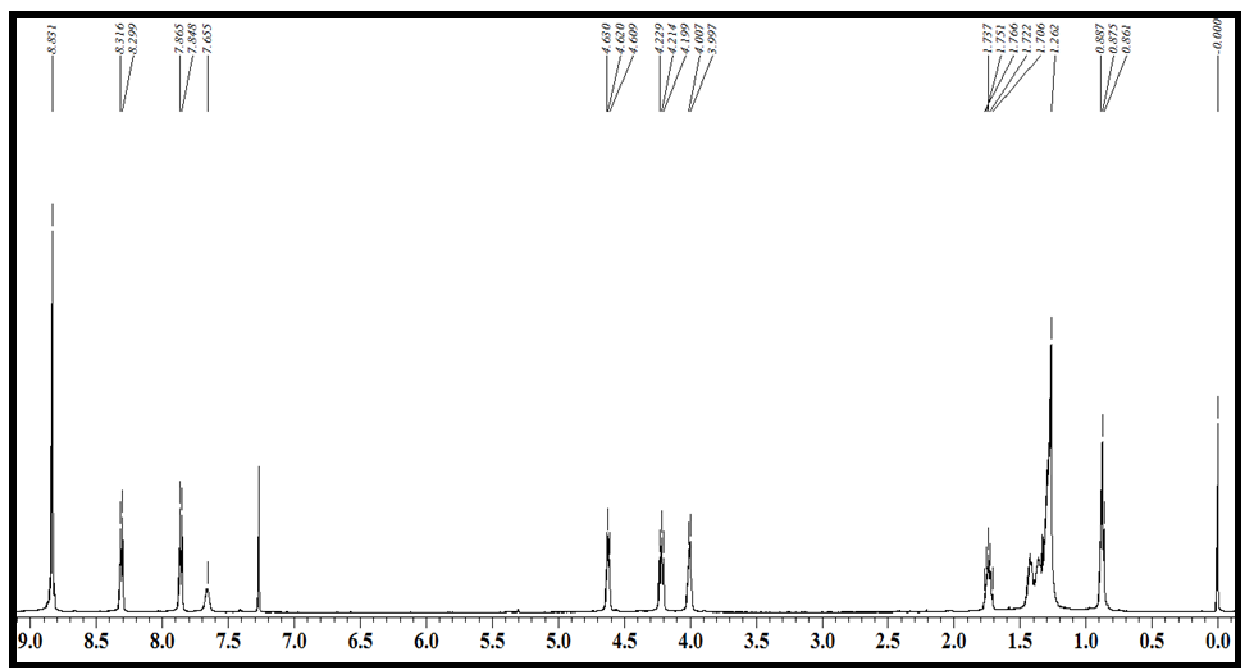


Figure S29. ¹H NMR (CDCl₃) of NDI-NA.

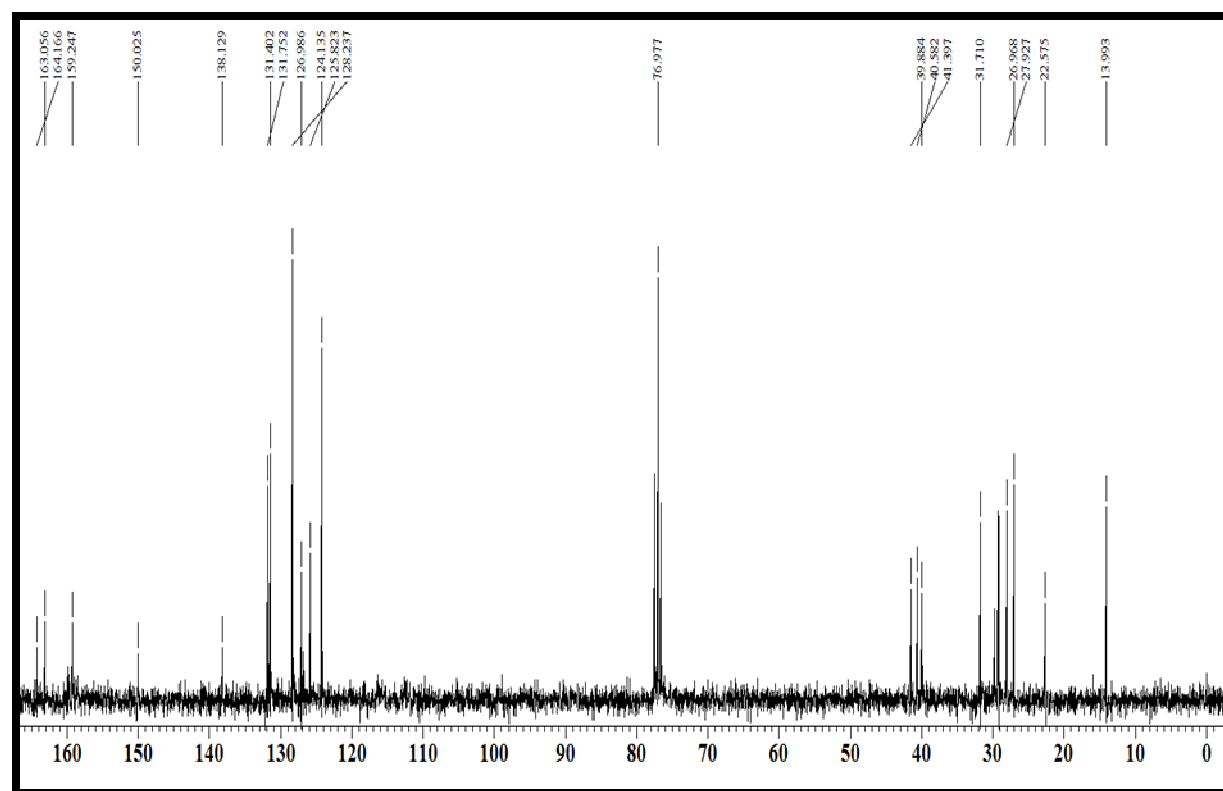


Figure S30. ¹³C NMR (CDCl₃) of NDI-NA.

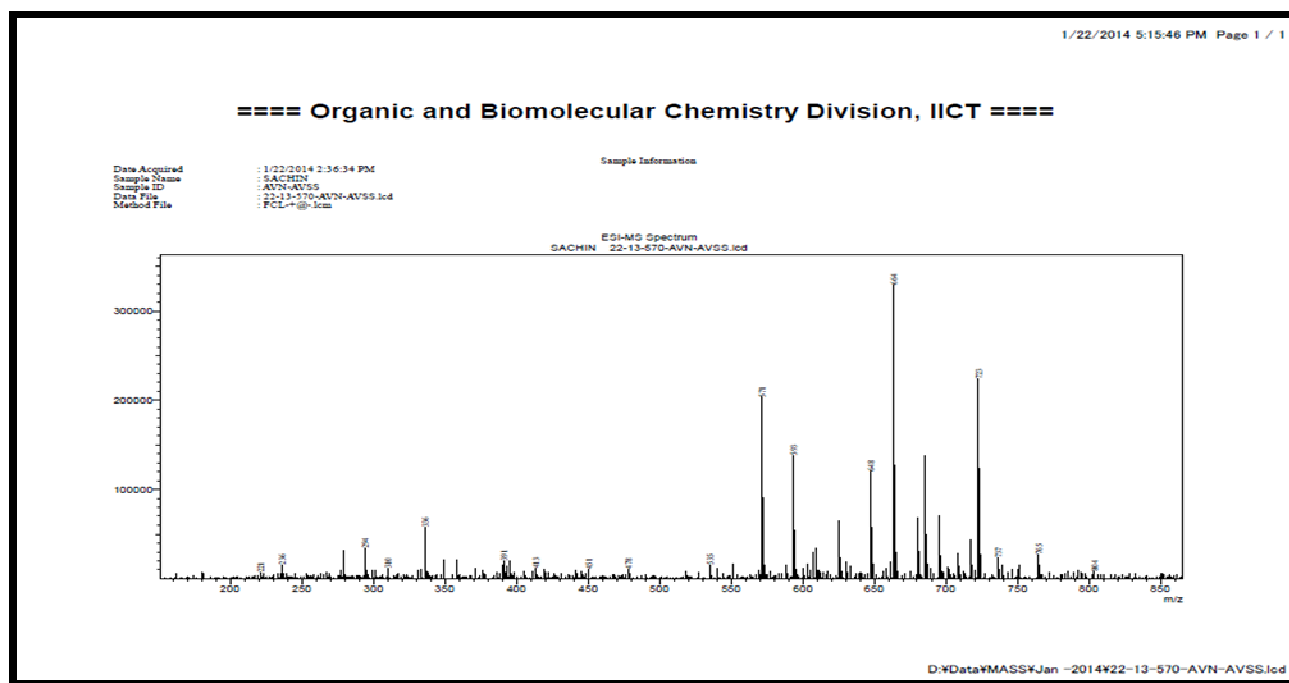


Figure S31. ESI MS ofNDI-NA.

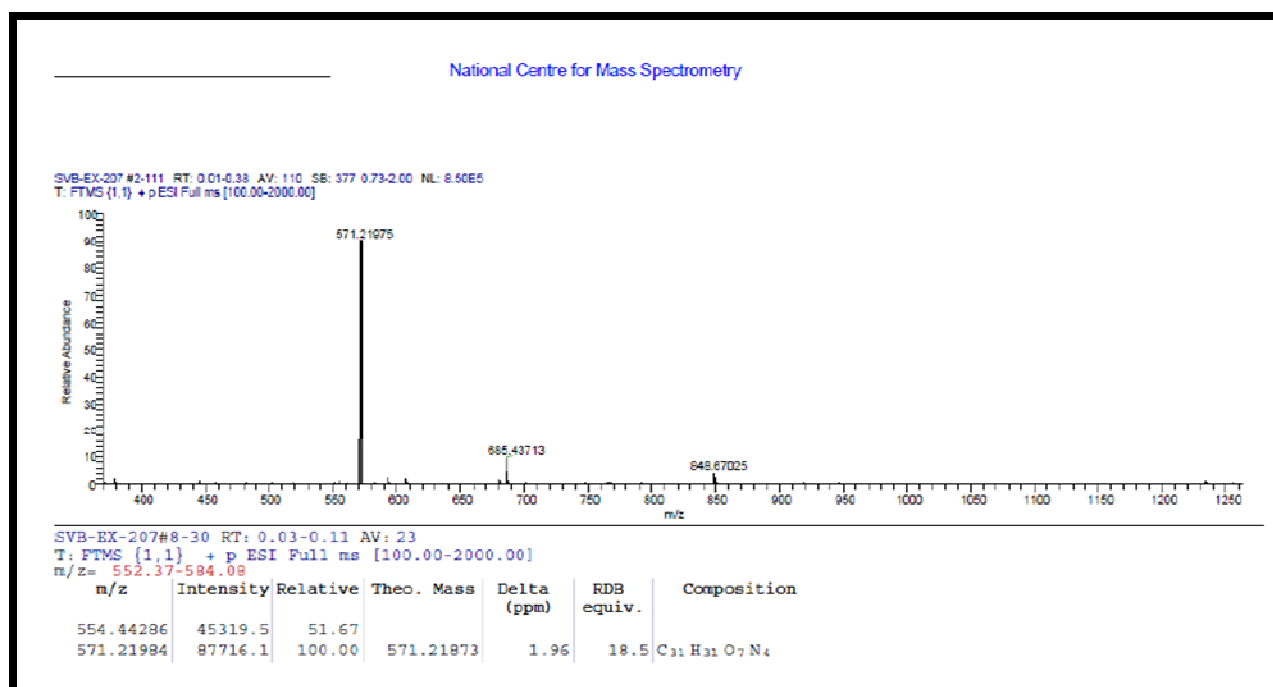


Figure S32. ESI-HRMS ofNDI-NA.